Electronic States and Magnetism of Mn Impurities and Dimers in Narrow-Gap and Wide-Gap III-V Semiconductors

W. H. Wang[1,2], Liang-Jian Zou[1,*] and Y. Q. Wang[1]

[1]*Key Laboratory of Materials Physics,*

Institute of Solid State Physics, Chinese Academy of Sciences,

P. O. Box 1129, Hefei 230031, China and

[2]*Graduate School of the Chinese Academy of Sciences*

(Dated: Nov 22, 2004)

Abstract

Electronic states and magnetic properties of single Mn impurity and dimer doped in narrow-gap and wide-gap III-V semiconductors have been studied systematically. It has been found that in the ground state for single Mn impurity, Mn-$As(N)$ complex is antiferromagnetic (AFM) coupling when p-d hybridization V_{pd} is large and both the hole level E_v and the impurity level E_d are close to the midgap; or very weak ferromagnetic (FM) when V_{pd} is small and both E_v and E_d are deep in the valence band. In Mn dimer situation, the Mn spins are AFM coupling for half-filled or full-filled p orbits; on the contrast, the Mn spins are double-exchange-like FM coupling for any p-orbits away from half-filling. We propose the strong p-d hybridized double exchange mechanism is responsible for the FM order in diluted III-V semiconductors.

PACS numbers: 75.50.Pp, 75.10.-b, 75.30.Hx

Diluted magnetic semiconductors (DMS), such as $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xN$, with ferromagnetic (FM) Curie temperature (T_c) as high as $110K$ in $Ga_{1-x}Mn_xAs$, or even as room temperature in $Ga_{1-x}Mn_xN$ have attracted much attention, since these properties provide perspective applications in the fabrication of spintronics devices as well as in quantum computers [1-5]. The unusual FM order in Mn- or Cr-doped III-V semiconductors with such low concentrated magnetic ions and the interesting magnetotransport properties have also raised many fundamental problems, e.g. the electronic states of $3d$ impurities and the origin of the FM long-range order (LRO) [2-4]. Many experiments have established the fact that local magnetic moments **S** and hole states are simultaneously introduced in DMS as Ga atoms are substituted by Mn ions. An elaborated relation between doped concentration and T_c in Ref.[1] demonstrated the important role of mobile hole carriers in the formation of FM LRO in DMS, leading to the hypothesis that the FM coupling between Mn spins are mediated through these delocalized holes.

Several microscopic mechanisms have been proposed to explain the origin of the carrier-induced FM LRO in DMS. In the presence of local magnetic ions and mobile carriers, the RKKY interaction seems to be a natural candidate [6]. Magnetic properties of $Ga_{1-x}Mn_xAs$ were interpreted in the RKKY scenario in the mean field (MF) approximation. Although the theory successfully explained the dependence of Curie temperature T_c and spontaneous magnetization on doping concentration measured in experiments in some doping range [7], there are still some important issues to be taken into account. The RKKY model validates only when isolated local spins merge in the sea of free carriers and the carrier bandwidth D is much greater than the spin-hole exchange constant J. However in DMS, the hole concentration n_h is much less than local spins concentration N_s, and the Mn-$As(N)$ spin-hole exchange constant, $J\sim$1eV, is much larger than the Fermi energy E_F of the hole carriers, about 0.3 eV [8]. Furthermore, the Mn concentration is so small that the nearest neighbour number z is less than that of the conventional 3-dimensional systems, thus it is expected that there will be a large discrepancy between the MF result and realistic situation. Therefore the MF RKKY theory might be not accurate for describing the FM ordering in DMS.

The double exchange model which is responsible for the FM order in doped perovskite manganites was also suggested for the FM coupling of the distant Mn spins in DMS [8, 9]. However, the spatial separation of Mn spins in DMS is much further than dense Mn spins in manganites, and the hole wavefunction extends over tens of lattice sites in doped $GaAs$

and the valence fluctuation in Mn 3d orbits is small, dissimilar to the mixed valence of $3d^3$ and $3d^4$ in doped manganites. At present, whether or not the conventional double exchange mechanism works for the nature of FM in DMS does not get strong support experimentally and theoretically. The polaronic mediated FM mechanism [10] and some other theories are also proposed to interpret the origin of FM LRO, which shows that more efforts are needed for the microscopic origin of the FM order in DMS.

One of the central problems in the debate on the microscopic origin of FM LRO in DMS is that the single impurity electronic states and the spin interaction of two magnetic ions, especially its evolution with various parameters of DMS, are not well understood. Single Mn impurity in III-V and IV semiconductors had been studied by Zunger et al. [11, 12] based on local density approximation and unconstrained MF approximation, substitutional impurity state properties of different transition-metal atoms in III-V semiconductors had also been studied in Ref.[13], the dependence of the impurity energy level on the nuclei charge of the transition metal atom had been known. The FM ground state (GS) in Mn doped DMS has also been confirmed by a lot of authors based on the first-principle electronic structure calculation, for example, see Ref.[14] and [15]. However these numerical studies are hard to clarify the microscopic processes of interacting Mn spins and the evolution of electronic states and magnetic properties of the Mn atoms and the host atoms in DMS with the doping concentration, the p-d hybridization strength, the energy gap of the host III-V semiconductors, the energy levels of the 3d impurities and the $4p$ holes, etc.. How these factors affect the FM ordering is crucial for our understanding of the unusual magnetism and transport in DMS.

The aim of this *Communication* is to elucidate the electronic states, the magnetic properties of single Mn-$As(N)$ complex, and the spin coupling between Mn spins for various parameters. In the rest of this *Communication*, after describing the model Hamiltonian, we first study the GS of single Mn-$As(N)$ for various electron configurations, determining the parameter range of the antiferromagnetic (AFM) coupling in the Mn-$As(N)$ complex; then we study the Mn-Mn spin couplings in the GS of two Mn-As(N) complexes,i.e. the Mn dimer, and show that the double-exchange-like mechanism is responsible for the FM order when the p-orbits of $As(N)$ is away from the half-filling, suggesting the intrinsic compensation of antisite defect or the inhomogeneity of hole distribution plays crucial roles.

For Mn doped III-V semiconductors with zinc-blende structure, such as In, Ga, or Al

for III group elements and As or N for V group elements, the five valence electrons of $As(N)$ occupies the four sp^3 dangling bonds with symmetry A_1 and T_2, the two $4s$ electrons of Mn ion covalently couple to the A_1 orbit of the As or N dangling bonds. When the divalent Mn impurity substitutes the trivalent In, Ga or Al as an effective mass acceptor, we now have a basic interaction scenario in DMS from various early experimental and theoretical studies: Mn ion contributes a spin and a hole, the spin localizes in Mn site, while the hole is bound to As or N site with an extension radius of r_s much larger than the lattice constant; the $3d$ electrons in Mn impurity interacts with the holes in the p orbits of surrounding As or N sites through hybridization V_{pd}, forming the Mn-$As(N)$ complex. Under T_d symmetry environment of the zinc-blende III-V semiconductors, the hole has equi-possibility to occupy the T_2 orbit in one of the four nearest-neighbour As or N sites around Mn ion, the hole is 4-fold degenerate; and in the T_d crystalline field, the $3d$ orbits of Mn ions split into lower energy E_g- like d orbits with pure atomic character and not coupling to As or N, and higher energy T_{2g}-like orbits coupling to the T_2 p orbit of As or N [13]. The Mn T_{2g} electron which hybridizes with the As or N hole is thus 3-fold degenerate. Due to the strong Hund's rule coupling, the hybridized $3d$ electron still couple with the local spin $\mathbf{S}$ ($S = 2$) of Mn $3d^4$ configuration via Hund's rule coupling J_H. The on-site Coulomb interactions between $3d$ electrons and between holes, U_d, and U_v, are also taken into account.

With the increase of doped Mn concentration, the wavefunctions of the holes centered at As or N atom with large radius r_s start to overlap with each other, the hopping integral between holes, V_h, crucially depends on the extension radius r_s and the hole density n_h. The Hamiltonian modeling the preceding physics in DMS thus reads:

$$\hat{H} = \sum_i \hat{H}_0(i) + \hat{H}_1 \tag{1}$$

$$\hat{H}_0(i) = \sum_\sigma (E_d \hat{d}_{i\sigma}^\dagger \hat{d}_{i\sigma} + E_v \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} + \frac{U_d}{2} n_{i\sigma}^d n_{i\overline{\sigma}}^d + \frac{U_v}{2} n_{i\sigma}^c n_{i\overline{\sigma}}^c)$$
$$- \frac{J_H}{2} \sum_{\mu\nu} \mathbf{S_i} \cdot \hat{d}_{i\mu}^\dagger \sigma_{i\mu\nu} \hat{d}_{i\nu} + \sum_\sigma V_{pd}(\hat{d}_{i\sigma}^\dagger \hat{c}_{i\sigma} + \hat{c}_{i\sigma}^\dagger \hat{d}_{i\sigma}) \tag{2}$$

$$\hat{H}_1 = \sum_{<ij>\sigma} V_h(\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma}) \tag{3}$$

where $H_0(i)$ and H_1 represent the interactions in the ith Mn-$As(N)$ complex and the inter-complexes hopping, respectively; E_d and E_v are the bare d-electron and p-orbit energy levels,
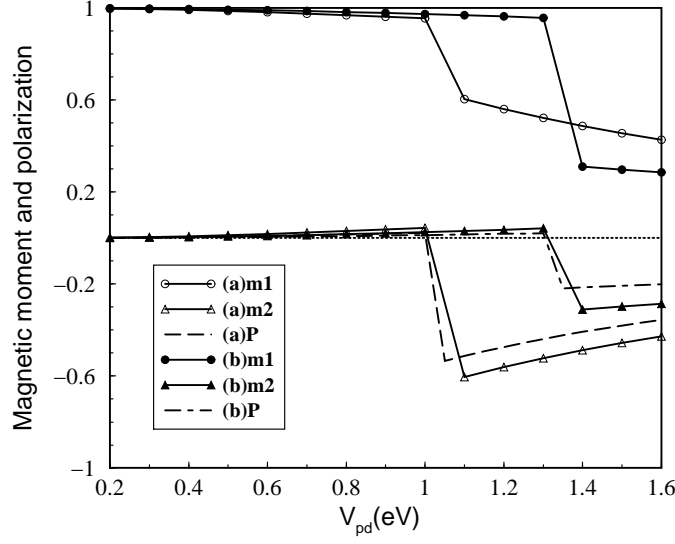
FIG. 1: Hybridization dependence of magnetic moment m_1, m_2 of the d, p electrons and spin polarization P of p electrons in the GS of $Mn - As(N)$ complex for (a) $GaAs{:}Mn$, E_v=-0.95 eV, E_d=-1.2 eV; (b) $GaN{:}Mn$, E_v=-1.8 eV, E_d=-0.5 eV. The other parameters: U_d=4.0 eV, U_v=0.35 eV, J_H=1.0 eV.

respectively; $\hat{d}_{i\sigma}^{\dagger}$ and $\hat{c}_{i\sigma}^{\dagger}$ denote the creation operators of the d electron and p electrons with spin σ in the ith $Mn - As(N)$ complex; we separate Mn $3d$ electrons into an inert local spin $\mathbf{S_i}$ of $3d^4$ configuration and a $3d$ electron which hybridizes with $4p$ orbit, the $3d$ electron couples with the local spin via strong Hund coupling; $n_{i\sigma}^{d}$ and $n_{i\sigma}^{c}$ denotes the electron occupation number of d state and p state with spin σ, and n=$\sum_{\sigma} n_{\sigma}^{c} + n_{\sigma}^{d}$ the total electron number; here U_v is usually much smaller than U_d [13]; unlike many other authors, we do not write our Hamiltonian as the simple Kondo lattice model, since we recognize that there exists strong pd hybridization between Mn $3d$ orbits and As or N p orbits, the $3d$ electron occupation varies with the pd hybridization, and the hole in the p orbit extends over a few of lattice constants, thus the Kondo lattice model is not proper to describe the physics in DMS. In this paper, we take the chemical potential μ located at the middle of the band gap, and the p- and d-levels E_v and E_d are taken with respect to μ. For clarity we neglect the degeneracy of Mn $3d$ electrons and p holes in the present study.

In the following we first present the electronic states and the evolution of single Mn impurity with the interaction parameters, and then the effective coupling between Mn spins of two Mn-As complexes in the DMS background.

A. Single Mn Impurity

We first study the electronic states of Mn and its ligand As or N atoms in the diluted limit, which describes the case that the distance of Mn ions is so far that the interaction between Mn impurities can be neglected, and no summation over lattice is needed in the Eq.(1)-(3). The local spin **S** is assumed to be aligned in the z axis, the electronic states and the magnetic properties of Mn-As complex are easily obtained by the exact diagonalization of H_0 for various physical parameter and electron configurations. As a contrast to the local moments formation in the Anderson impurity model, the p-electron is AFM polarized as the p-d hybridization V_{pd} is stronger than a critical value V_c, as seen in Fig. 1. When V_{pd} is small, $V_{pd} < V_c$, we find that in the GS the p orbit is almost full filled and the electrons in each p orbit are positive polarized weakly. The p and d electron occupations are almost fixed for $V_{pd} < V_c$. The maximized polarized moment of each As or N are about $0.026\mu_B$ for $GaAs$:Mn and $0.042\mu_B$ for GaN:Mn as $V_{pd} \to V_c$. A small fraction of spin-down p electron transfers to $3d$ orbit, which leads to the weak positive polarization of the p orbit and $S \approx \frac{5}{2}$ at Mn site. As V_{pd} increases to $V_c \approx 0.88eV$ for $GaAs$:Mn or $\approx 1.33eV$ for GaN:Mn, the holes strongly hybridize with the $3d$ electron, a large fraction of d electron transfers to the p orbit, leading to the AFM alignment of the p electron in respect to the d electron. This result is in agreement with the magnetic circular dichroism experiment [16]. The corresponding polarization of the As or N atoms around Mn impurity, is also shown in Fig.1. The maximum polarized magnetic moment of each $As(N)$ is about $-0.58\mu_B$ for $GaAs$:Mn and $-0.32\mu_B$ for GaN:Mn. Our result for GaN:Mn is in good agreement with that obtained by the first-principles electronic structure calculation in Ref. [17] for Mn-N cluster, but considerable larger than that in periodic systems [18]. While, considering the four equivalent As or N atoms around the Mn ion, we expect the polarized moment of each As or N atom is smaller than this value.

The dependence of the magnetic moment and the polarization of the p orbits on the $3d$ energy level E_d is very similar to that on the hybridization V_{pd} in Fig.1. For deep $3d$ energy level E_d, the p electrons in p orbits are positively polarized and very weak; there also exists a critical value E_d^c that when E_d is shallower than E_d^c, the electrons in the p orbits are AFM polarized, the polarization of the p orbit is about -40% for $GaAs$:Mn or -20% for GaN:Mn. Since the hole is located around the top of valence band, the closer
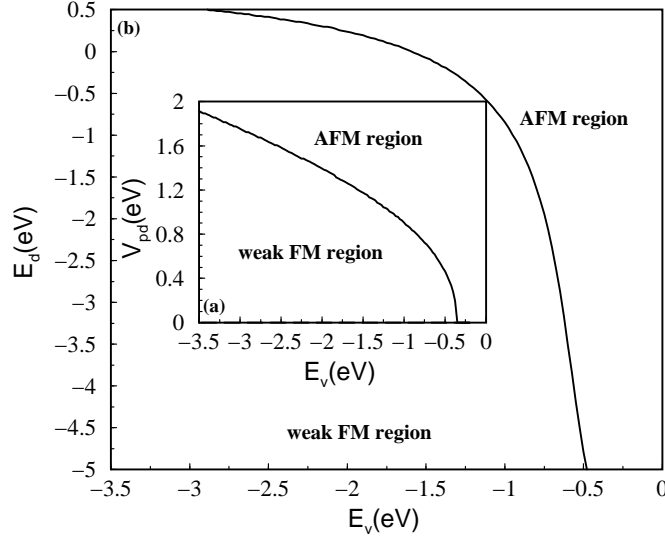
FIG. 2: The phase diagram of Mn-$As(N)$ complex (a) V_{pd} vs E_v, E_d=-0.5 eV and (b) E_d vs E_v, V_{pd}=1.0 eV. The other parameters are the same in Fig.1.

the E_d is to E_v, the larger the p-d hybridization is, hence more strong polarization of the p electron. Too deep or too shallow E_d level is not favorable of the formation of the AFM Mn-$As(N)$ complex. In the GS for $V_{pd} = 1.0eV$, the energy difference between FM and AFM configurations of Mn-$As(N)$ complex is $-0.93eV$ for $GaAs$:Mn and $-1.26eV$ for GaN:Mn. The former agrees with the photoemission data obtained by J. Okabayashi et al. [19].

The magnetic phase diagrams of single Mn-$As(N)$ complex on V_{pd} vs E_d and vs E_v are shown in Fig.2a and Fig.2b. The common character of the phase diagrams is there exist very weak FM and AFM polarized regions. We find when both E_d and E_v are very deep, the electrons in the p orbits are not polarized, i.e. the paramagnetic region, this region is not shown in Fig.3; as E_d and E_v are lifted, the p electrons become weak FM polarization to the Mn spin; and for large enough V_{pd} and shallow E_d or E_v, the p electrons in As or N site are AFM polarized. In fact, the physical parameters in realistic DMS $GaAs$:Mn and GaN:Mn fall into the AFM region, this provides such a possibility that the Mn spins interact through AFM polarized As or N ligands to form FM correlation. As we showed in the following, the Mn spins establish double-exchange-like FM correlation via the polarized p-d hybridized band.
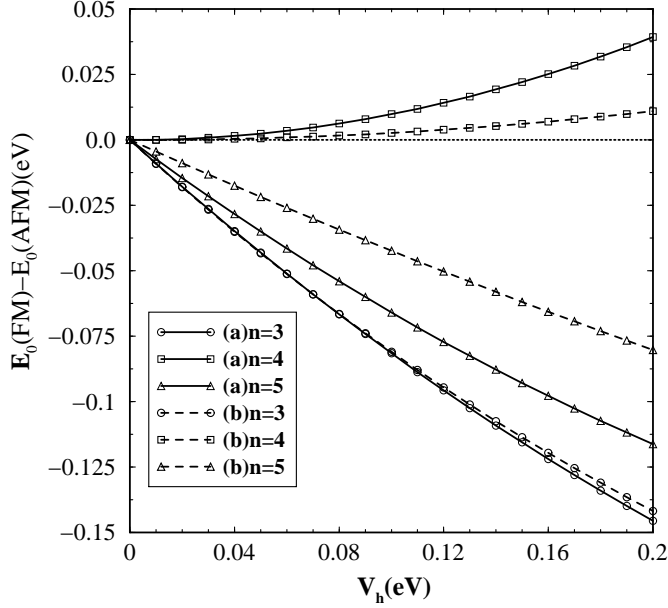
B. Mn Dimers

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FIG. 3: The ground state energy difference between Mn-Mn FM coupling and AFM coupling $vs.$ V_h in $(Mn - As)$ dimer for (a) $GaAs$:Mn and (b) GaN:Mn, V_{pd}= 1.0eV. The other parameters are the same in Fig.1.

Next we consider two Mn-$As(N)$ complexes, and study the GS magnetic configuration and the spin coupling between Mn ions. With the increasing of Mn doping density and hole concentration, the separation between holes becomes smaller and smaller, the wavefunctions of these holes begin to overlap. The hopping integral between two overlapped holes at sites $\mathbf{R_i}$ and $\mathbf{R_j}$ is depicted by $V_h(i,j) = < \psi_h(\mathbf{R_i})|h_0|\psi_h(\mathbf{R_j}) >$, here $\psi_h(\mathbf{R_i})$ is the hole wavefunction and h_0 is the Hamiltonian of single particles. We approximate ψ_h with the hydrogen-like wave function with radius r_s and effective mass m^*. In this situation, the summation of lattice in Eq.(1)-(3) runs over indices 1 and 2. For simplify, the core spins of two Mn ions are assumed semiclassical and the spin $\mathbf{S_2}$ deviates an angle of θ with respect to $\mathbf{S_1}$.

In the GS of Mn dimer, the Mn core spins are either strong FM or weak AFM coupling, depending on the electron filling the p-orbits, as shown in Fig.3. Comparing the GS energy of the Mn dimer of FM configuration with that of AFM configuration, we find that Mn-Mn AFM configuration is stable for the half- or full-filled p-orbits in the two As or N sites, however, FM is more stable when the electron filling in the As or N p orbit deviates from half- or full- filling; and the more the hole number is, the stronger the Mn-Mn FM coupling is. The magnetic coupling strength of the Mn dimer monotonically increases with

the hopping integral V_h and the AFM coupling strength is much less than the FM coupling strength, which can be clearly seen in Fig.3

With the substitution doping of Mn to Ga, core spins and holes are introduced simultaneously in the semiconductor host. Formally the density of Mn spins equals to the hole concentration. It seems that the active p orbits is always half-filled. For the half-filled Mn dimer, the opposite spin alignment of the different p orbits, the AFM coupled p-d hybridization, the strong Hund's coupling between the $3d$ electron and the local spin lead to AFM coupling of the Mn local spins. However, considering the existence of numerous antisite As and the intersite Mn defects, a significant fraction of holes are compensated by the electrons from these defects. Thus the hole concentration is considerable less than the Mn density, the $n = 5$ electron configuration in the $(Mn$-$As)$ dimer is the most probable in realistic DMS. In the GS with electron configuration away from half-filling, the hopping of holes and their AFM hybridization with $3d$ electrons lead to the FM coupling between Mn $3d$ electrons, hence the FM coupling of Mn-Mn spins, just as our prediction for $GaAs$:Mn and GaN:Mn.

To further understand the nature of FM LRO in DMS, we study the GS total energy on the azimuthal angle θ between two local spins for various electron filling, and the result is shown in Fig.4. The total energies $E(\theta)$ are measured relative to the Mn-Mn AFM configuration. We notice that for the half-filling case, the energy difference exhibits $\cos\theta$ behavior, indicating that the Mn-Mn coupling is Heisenberg-like AFM. In contrast, in the case deviating from half-filling, the GS energy difference can be well fitted by $|\cos\frac{\theta}{2}|$, and this character is very similar to doped manganites, which implies that the Mn-Mn FM coupling is double-exchange-like. This outstanding behavior seems to conflict with what we fore-mentioned. In fact, in the present scenario of strong hybridization with p orbit and strong Hund's coupling with core spin in the DMS, the d-electron form a narrow itinerant band, so the physical interaction of Mn spins in proper doping DMS quite resembles double exchange interaction in mixed-valence manganites. The FM coupling energy of two Mn spins in $GaAs$:Mn is about 11 meV, comparable with experimental Curie temperature T_c. In GaN:Mn the FM coupling energy is about 75 meV, it seems plausible to explain the origin of extremely high Curie temperature $T_c \approx 600 - 900K$ in wide-gap GaN:Mn.

We find in AFM polarized Mn-As and Mn-N, the polarized magnetic moment at As site is larger than that at N site, this occurs both for single complexes and for dimers; on
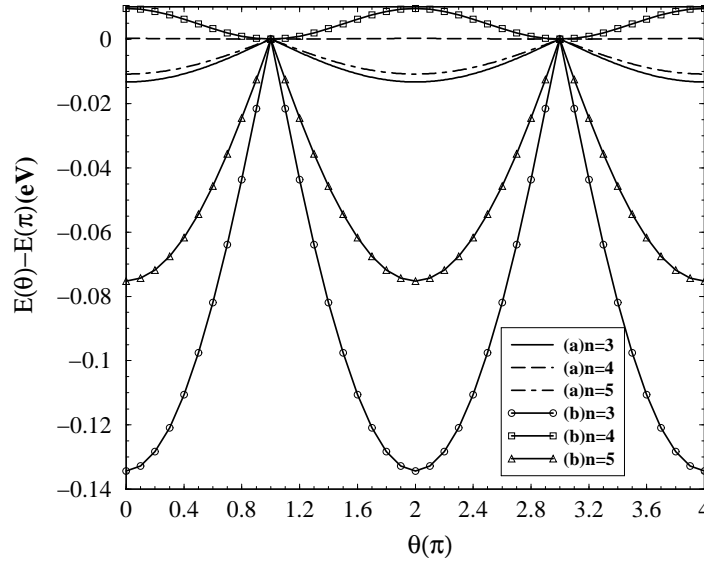
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FIG. 4: The θ dependence of ground-state energy difference in two $(Mn$-$As)$ complexes for (a) $GaAs$:Mn, $V_h \approx 0.015 eV$ and (b) GaN:Mn, $V_h \approx 0.186$ eV. The other parameters are the same in Fig.3.

the contrary, the FM coupling energy of the Mn spins in $GaAs$:Mn is smaller than that in GaN:Mn. This arises from that the charge transfer of the spin-up $3d$ electron to the p-orbit in Mn-As is less than that in Mn-N; however, the hopping integral of the holes in the latter is larger than the former, leading to more wider hybridized d-band in the latter and contributing more strong double-exchange FM coupling strength. From Fig.3 and Fig.4, one find that the more the hole number is, the stronger the Mn-Mn magnetic coupling is, implying that the presence of more holes favors the FM in DMS. The observation of FM ordering in DMS suggests that antisite As or intersite Mn atoms may compensate a significant fraction of holes, leading to the observed double-exchange-like FM coupling strength. Also, the possible inhomogeneous distribution of the hole density could lead to the FM phase, since even in the molecular-beam epitaxy grown DMS thin films inhomogeneous strain was found to widely exist in most of DMS samples, this favors the inhomogeneous distribution of the holes. With the coexistence of both the $n=3$ and the $n=5$ electron configurations, lower magnetic energy and inhomogeneous distribution of FM coupling are expected in the GS.

As we mentioned in the preceding, the Mn local spins in DMS is so distant in comparison with dense spins in doped manganites that one may question the role of the double exchange

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mechanism in DMS. The microscopic mechanism for the double exchange FM in Mn-doped DMS is depicted as follows: due to the strong hybridization of the $As(N)$ p orbits with the 3d electrons, the system forms two hybridized narrow bands; the hybridized band with dominant d orbital character couples to the Mn core spins via strong Hund's rule coupling, thus the hopping of the mobile electrons between localized Mn spins gives rise to the double-exchange-like FM coupling and leads to the FM order in DMS, similar to that in doped manganites.

Compare the present double-exchange-like FM with the conventional double exchange FM in manganites, we find the valence fluctuation in the FM ordered DMS is significantly less than that in doped manganites. Due to the strong p-d hybridization and the extended wavefunctions of the p holes, the lifetimes of the mobile electrons staying around two local spins are nearly equal, therefore one would not expect strong valence fluctuation in Mn 3d orbits. Meanwhile, the Curie temperature in DMS seems to be too high in comparison with the FM critical temperature in manganites, this may attribute to that the strong Jahn-Teller e-ph coupling and polaronic effect weaken the FM phase transition point in manganites.

In summary, we have shown that in doped III-V semiconductors, Mn-$As(N)$ is AFM polarized only for strong p-d hybridization; the Mn-Mn spin interaction is double-exchange-like ferromagnetic coupling, addressing the strong ferromagnetism in diluted magnetic III-V semiconductors. The consideration of the p-orbital degeneracy will lead to more reasonable polarized magnetic moment and polarization at As or N site.

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